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COMMUNICATIONS

State to state recoil anisotropies in the photodissociation of deuterated ammonia

David H. Mordaunt,[a] Michael N. R. Ashfold,[b] and Richard N. Dixon
School of Chemistry, University of Bristol, Bristol, BS8 1TS, United Kingdom

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The near ultraviolet photodissociation of deuterated ammonia, ND_3, allows particularly clear observation and quantification of the quantum state dependent angular anisotropy of the recoiling $D+ND_2(\tilde{X})$ photoproducts. The recoil anisotropy is shown to depend upon five quantum numbers: The rotational quantum numbers of the parent molecule selected in the absorption process, and the rotational and vibrational quantum numbers of the resulting products. © *1998 American Institute of Physics.* [S0021-9606(98)01742-5]

We report studies of the photodissociation of deuterated ammonia (ND_3) molecules which provide a particularly clear demonstration that the recoil angular anisotropy of the $D+ND_2(\tilde{X})$ products is a sensitive function both of the parent rotational quantum numbers selected in the absorption process and of the resulting product rotational and vibrational quantum numbers. Theory[1] has long predicted such quantum state dependent product recoil anisotropies, but their experimental demonstration remains rare.

Classically, the spatial angular distribution of the recoiling photofragments resulting from molecular photodissociation brought about using linearly polarized light is given by

$$I(\theta)=\frac{1}{4\pi}[1+\beta P_2(\cos\theta)]. \tag{1}$$

where β is the classical anisotropy parameter, θ is the polar angle between the velocity vector, v, of the recoiling fragment and the electric vector, ϵ, of the photolysis laser, and P_2 the second-order Legendre polynomial $\{P_2(x)=\frac{1}{2}(3x^2-1)\}$.[2,3] Measurement of β can shed light on the character of the electronic transition dipole moment, μ, and on the time scale of the dissociation process. In the limit of a prompt dissociation of a linear molecule, β takes values of $+2$ or -1 according to whether μ is aligned parallel or perpendicular to the dissociating bond [i.e., from Eq. (1), the fragments recoil with a $\sin^2\theta$ or $\cos^2\theta$ distribution, respectively]. Rotation of the excited molecule prior to fragmentation averages the angular dependence, partially degrading the angular distribution so that it becomes more isotropic (i.e., β tends towards zero). The present work illustrates additional factors quantifying the recoil anisotropy in terms of the excitation and fragmentation processes. The quantum recoil anisotropy parameter $\beta(\alpha)$ is shown to be dependent upon five quantum numbers which, for simplicity, we denote collectively as α pending detailed discussion below.

Photodissociation processes that are fully state resolved, both in the parent molecule and in the resulting products, provide some of the most detailed insight possible into the dynamics of molecular photofragmentation processes. Dissociation of ND_3 via the origin band of its $\tilde{A}\ {}^1A_2''-\tilde{X}\ {}^1A_1'$ electronic transition is one such system. The $\tilde{A}-\tilde{X}$ absorption spectrum exhibits a long progression in ν_2', the excited state out of plane bending mode—a direct consequence of the Franck–Condon principle and the planar ← pyramidal change in equilibrium geometry that accompanies this electronic transition. The spectroscopy of this transition is well established.[4] The $\tilde{A}$ state is predissociated, to the extent that the jet-cooled absorption spectrum of NH_3 shows vibrational but no rotational structure; the advantage of studying the fully deuterated isotopomer (ND_3) is that it predissociates sufficiently slowly that its $\nu_2'=0\leftarrow\nu''=0$ and $\nu_2'=1\leftarrow\nu''=0$ bands show resolved rotational structure, as illustrated in Fig. 1. Thus by judicious choice of excitation wavelength we can specify the rotational quantum numbers of both the initial and final states of the parent ND_3 molecule. The only energetically allowed fragmentation pathway for ND_3 molecules following excitation to the $\tilde{A},\nu'=0$ level is D atom elimination following cleavage of a D–ND_2 bond.

The photodissociation of ND_3 is investigated experimentally using the technique of D atom photofragment translational spectroscopy[5] which offers sufficient energy resolution to reveal the rovibrational quantum state population distributions within the partner ND_2 photofragments. Two photolysis energies are chosen: 46 708 and 46 724 cm^{-1}, appropriate for excitation of, respectively, the $Q_1(1)$ [and, to a lesser extent, $Q_1(2)$] and $R_0(0)$ transitions within the $ND_3(\tilde{A}-\tilde{X})$ origin band. The resulting D atom photofragments are tagged, state selectively, prior to escaping the interaction region, by a two-color two-photon electronic excitation scheme ($\lambda=121.6$ nm and $\sim$365.6 nm, respectively) resulting in population of a Rydberg state with principal quantum number, $n\sim 80$. The D atom translational energies and thus, by momentum conservation, the total fragment kinetic-

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[a] Present address: Coherent Inc., Medical Group, 2400 Condensa Street, Santa Clara, CA 95051.

[b] Electronic mail: mike.ashfold@bristol.ac.uk

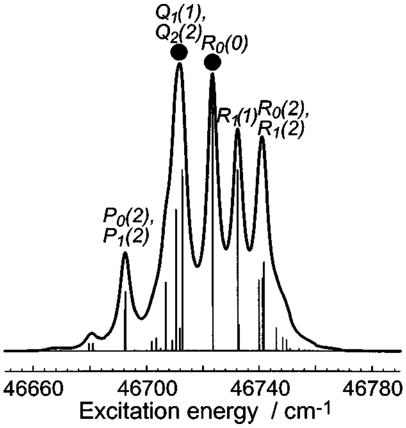

FIG. 1. Simulated absorption spectra of the $ND_3(\tilde{A}-\tilde{X})$origin band assuming a parent rotational temperature of 15 K (but a 300 K nuclear spin temperature) and a lifetime broadened transition width of 4.2 cm^{-1} (Ref. 4), together with a stick spectrum indicating the contributing transitions. The full circles (●) indicate the transitions chosen for investigation.

energy release (E_T), are determined by measuring the D atom times of flight to a detector mounted 825 mm distant along the axis orthogonal to the plane containing the molecular beam and the photolysis and tagging laser beams.

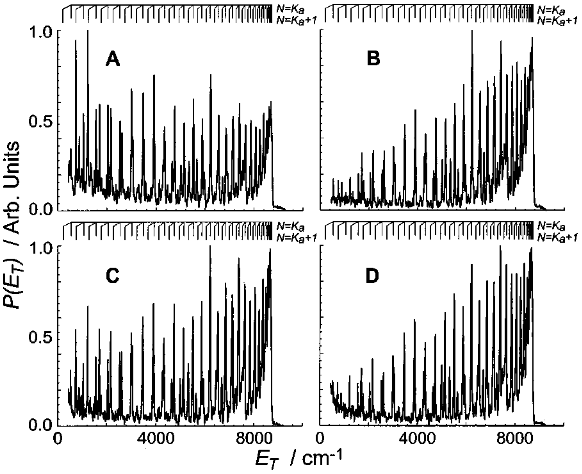

FIG. 2. D+ND_2 photofragment translational energy distributions, $P(E_T)$, resulting from dissociation of ND_3 following excitation via the $\tilde{A}-\tilde{X}$,(0,0),$R_0(0)$, and $Q_1(1)$ transitions with the detection axis respectively parallel (A) and (C) and perpendicular (B) and (D) to the laser polarization axis. Combs superimposed above the spectra indicate the various populated rotational levels of $ND_2(\tilde{X})_{v=0}$.

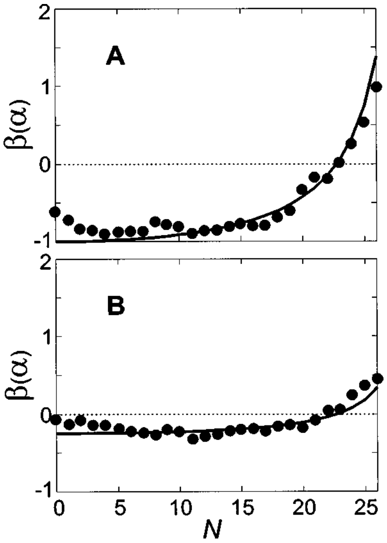

FIG. 3. Experimentally resolved (●) and theoretical predicted [—, by Eq. (5)] anisotropy parameters for photodissociation of $ND_3(\tilde{A})_{v=0}$ molecules following preparation via the (A) $R_0(0)$ and (B) $Q_1(1)$ transitions.

As Fig. 2 shows, the $P(E_T)$ spectra exhibit structure reflecting the energies of the various quantum states of the ND_2 partner fragment that are populated in the fragmentation process. Analysis shows that nearly all the ND_2 fragments are formed with only zero-point vibrational energy, but with a high degree of rotational excitation. This rotational excitation is concentrated about the *a*-inertial axis (i.e., states with product rotational quantum numbers $N=K_a$ and $N=K_a+1$). Such observations are consistent with previous discussions of the dissociation dynamics of ammonia.[5–7] The relative populations of these product states are deduced from the intensities of the corresponding peaks in the $P(E_T)$ spectrum. Thus the experiment yields a one-dimensional (1D) radial cut through the three-dimensional (3D) recoil distribution. The angular distributions are obtained by rotating the ϵ vector of the photolysis laser radiation so as to sample both parallel and perpendicular orientations with respect to the detection axis. Clearly, the detailed intensity distributions observed are sensitive both to the alignment of ϵ [compare Figs. 2(A) with 2(B), and Figs. 2(C) with 2(D)] and to the detail of the parent rovibronic transition excited [compare Figs. 2(A) with 2(C) and Figs. 2(B) with 2(D)]. The recoil angular anisotropy parameter may be determined experimentally, as a function of product ND_2 vibrational and rotational quantum states, via the relationship

$$\beta(\nu,N)=2\frac{I_{\text{para}}(\nu,N)-I_{\text{perp}}(\nu,N)}{I_{\text{para}}(\nu,N)+2I_{\text{perp}}(\nu,N)}. \qquad (2)$$

where $I_{\text{para}}(\nu,N)$ and $I_{\text{perp}}(\nu,N)$ represent the relative population of the ND_2 photofragment with vibrational and rotational quantum numbers ν and N, measured with ϵ parallel and perpendicular to the detection axis.

The most striking aspect of the present work is the quantitative measure of the state selective recoil anisotropy parameter, $\beta(\alpha)$, obtained using Eq. (2). Two effects are clearly apparent from the plots shown in Fig. 3. First, the magnitude of $\beta(\alpha)$ depends sensitively upon the initial rotational state of the parent molecule from which dissociation occurs. Second, the value of $\beta(\alpha)$ is not constant for all of the product quantum states, but varies from a negative value for low N levels of ND_2 to a positive value for levels with high $N\sim K_a$. The full recoil angular distributions resulting from photodissociation through these two different parent transitions are reconstructed in Fig. 4. The concentric circles represent the flux of ND_2 photofragments with a given rotational quantum number $N\sim K_a$, and thus a given recoil velocity and kinetic energy. The $\tilde{A}$ state of ammonia has a trigonal planar geometry with the $\tilde{A}-\tilde{X}$ transition dipole moment parallel to the C_3 axis. The laser preferentially excites molecules aligned with their transition dipole aligned parallel to ϵ, i.e., with their molecular plane perpendicular to the laser polarization. For

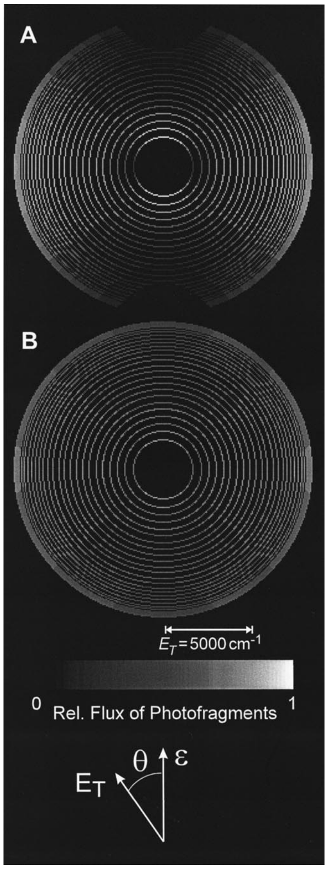

FIG. 4. Polar plot illustrating a 2D cut through the 3D distribution of $\mathrm{D}+\mathrm{ND}_2(\tilde{X})_{\nu=0}$ product recoil energies arising in the photodissociation of ND_3 molecules following excitation on the (A) $R_0(0)$ and (B) $Q_1(1)$ transitions of the $\tilde{A}-\tilde{X}(0,0)$ band derived from the experimental measurements displayed in Figs. 2 and 3. The radial axis is product translational energy, the ϵ vector of the photolysis laser is vertical, and the angle is between ϵ and the recoil axis. Azimuthal symmetry is assumed about the laser polarization axis. The bare central region in each plot reflects the inability of the time-of-flight experiment to monitor the slowest D atom products.

excitation via the $R_0(0)$ transition, D atoms formed with ND_2 products appearing in low N levels preserve this alignment with maximum flux orthogonal to the laser polarization; however, as the value of N increases the trend is reversed, with the maximum flux of photofragments appearing parallel to the laser polarization axis. For excitation via the $Q_1(1)$ transition the recoil distribution for all ND_2 product levels is more isotropic, however, there is a small anisotropy following the same trend as for the $R_0(0)$ transition, as indicated by the $\beta(\alpha)$ values in Fig. 3.

The lifetime of ND_3 molecules in their $\tilde{A}, \nu'=0$ state that result from excitation via the $R_0(0)$ and $Q_1(1)$transitions is ~2.7 ps.[4] This lifetime exceeds its rotational period (~2.2 ps for molecules with $N'=1$). Thus the excited molecules typically make at least one complete rotation prior to dissociation. Classically, we would expect this to degrade the photofragment recoil anisotropy, thereby tending towards an isotropic recoil distribution. Clearly this is not the case, the excited molecules remain aligned and the degree of the alignment is dependent upon the particular parent rotational transition excited.

For a molecule that dissociates on a time scale longer than its rotational period, the degree of spatial alignment can be described by the alignment parameter, $A_0(J',J'',K)$. The photofragment recoil anisotropy can then be expressed as

$$\beta(\alpha)=A_0 P_2(\cos\chi), \tag{3}$$

where χ represents the angle between the transition dipole and the dissociating bond. The $\tilde{A}-\tilde{X}$ transition in ammonia is parallel, thus there are three important quantum numbers: The projection of the total angular momentum on the C_3 top axis (K_c, henceforth denoted simply as K for both initial and final states), and the initial and final rotational angular momenta (J'' and J'). The $A_0(J',J'',K)$ value is dependent on the specific rotational transition selected, i.e.,

$$A_0(J',J'',K)=(-1)^{J'+K}\sqrt{30}(2J'+1)\begin{pmatrix} J' & J' & 2 \\ K & -K & 0 \end{pmatrix} \times \begin{Bmatrix} J'' & J' & 1 \\ 2 & 1 & J' \end{Bmatrix}, \tag{4}$$

where ( ) and { } denote 3-$j$and 6-j symbols, respectively.[3,8] The rotationally resolved $R_0(0)$ and $Q_1(1)$transitions have $A_0(J',J'',K)$ values of +2.0 and +0.5, respectively, notwithstanding the fact that $J'=1$in both cases. At this point, since $\chi=90°$, we would thus predict that the products of the dissociation of ND_3 from these particular excited-state levels should yield constant anisotropy parameters $\beta(\alpha)$ of -1.0 and -0.25, respectively.

We also observe that the photofragment recoil anisotropy parameter is dependent on the product rotational quantum number ($N \sim K_a$). The D atom ejected by molecules that dissociate to yield ND_2 fragments with low rotational angular momentum are preferentially directed in the plane of the excited molecule [i.e., perpendicular to μ, with $\beta(N=0 \sim -\frac{1}{2}A_0(J',J'',K)$ as predicted by Eq. (3)]. Conversely, the D atoms formed in association with the most highly rotationally excited ND_2 partners tend to recoil almost parallel to the transition dipole, i.e., $\beta(N=K\sim 26)\rightarrow A_0(J',J'',K)$. such dynamics are a consequence of the conical intersection between the $\tilde{A}$ and $\tilde{X}$ state potential-energy surfaces, at planar geometries, in the D–ND_2 dissociation coordinate, which gives rise to a large out of plane torque.[9,10] Products with a small degree of rotational excitation arise from fragmenting parent molecules with internuclear trajectories which pass through the conical intersection without experiencing this torque, and behave as predicted by Eq. (3). However, products with considerable rotational excitation have been accelerated by the torque tangential to the molecular plane, this enhances the rotational motion and perturbs the recoil anisotropy. The measured energy and angular momentum disposal within the products are reproduced well by an impact parameter model,[6] which predicts the quantum recoil anisotropy for each product N state

$$\frac{\beta(\alpha)}{A_0(J',J'',K)}=\frac{3N(N+1)\hbar^2}{2\mu R_{TS}^2 E_T(N)}-1. \tag{5}$$

The model assumes that the transition state for dissociation is located at the conical intersection. The reduced mass (μ) and bond distance (R_{TS}) of the departing D atom are evaluated at the conical intersection. $E_T(N)$ denotes the translation energy release for the product quantum states. As Fig. 3 shows, these calculated values of $\beta(\alpha)$ are in excellent accord with those obtained from experiment, confirming this dynamical interpretation.

In conclusion, the quantum anisotropy parameter is dependent on five quantum numbers, such that $\beta(\alpha) \equiv \beta(J',J'',K;N)$. Ammonia is the first molecule for which such detailed quantum effects in product recoil anisotropies have been observed and quantified. The state dependence of $\beta(J',J'',K;N)$ is brought about by two processes: First optical excitation (which determines the alignment of the parent molecular frame in the laboratory frame of reference); second, the dissociation dynamics (which can be dependent on product quantum state).

Finally, it is worth commenting on the generality of such observations. The creation and retention of significant alignment in these ND_3 molecules, notwithstanding their predissociating on a time scale longer than the rotational period, is a consequence of the pure parent state selection (excitation of a range of J',K' levels would result in a more isotropic ensemble of excited-state molecules) and the lack of suitable (Coriolis) couplings by which the well defined precession might be scrambled. Both of these necessary attributes will generally be harder to achieve in heavier, more predissociated systems (where spectral congestion would be more problematic) or in molecules carrying higher levels of internal excitation. The observation of a dramatic product quantum state dependence of $\beta(\alpha)$ also requires a rather favorable set of circumstances. For example, in the case of ammonia, we picture the ultimate energy disposal as being established in a very confined region of configuration space (the conical intersection) and a well defined mapping of the extent of some parent motion orthogonal to the dissociation axis at this transition state (out of plane bending in this case) onto the eventual product quantum states. Although the quantum state sensitivity of the spatial anisotropy parameter $\beta(\alpha)$ is readily understandable and predicted theoretically, clear experimental demonstrations are likely to remain rather elusive.

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